

# Heat Capacity and Thermodynamic Properties of $\beta$ -Lithium Hexafluoroaluminate, $\text{Li}_3\text{AlF}_6$ , from 15 to 380 K\*

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The heat capacity of  $\beta$ -lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$ , was determined from 15 to 380 K and the thermodynamic properties calculated from the results. The entropy at 298.15 K was found to be  $187.88 \pm 0.38 \text{ J/K} \cdot \text{mol}$  ( $44.904 \pm 0.090 \text{ cal/K} \cdot \text{mol}$ ).

Key words: Calorimetry; entropy; heat capacity;  $\beta$ -lithium hexafluoroaluminate; thermodynamic properties.

## 1. Introduction

The heat-capacity measurements on  $\beta$ -lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$ , have been obtained between 15 and 380 K as a part of the research program at the National Bureau of Standards to provide accurate thermodynamic data on light-element compounds. The specimen employed in the measurements was a portion of the same  $\text{Li}_3\text{AlF}_6$  preparation from which the sample had been taken for the previously reported relative enthalpy measurements between 273.15 and 1073.15 K by Douglas and Neuffer [1].<sup>1</sup>

The phase diagram of the lithium fluoride–aluminum fluoride binary system shows one congruent melting compound, lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$  [2, 3]. As observed in other compounds of composition  $\text{M}_3\text{AlF}_6$  of the alkali fluoride–aluminum fluoride system [4], the  $\text{Li}_3\text{AlF}_6$  also exhibits polymorphism. Five crystalline forms have been reported between room temperature and the melting point (1056 K) [5, 6, 7]. When  $\gamma$ - $\text{Li}_3\text{AlF}_6$  is cooled slowly to room temperature from about 600 °C,  $\beta$ - $\text{Li}_3\text{AlF}_6$  is obtained; when the sample is quenched from about 600 °C to room temperature,  $\alpha$ - $\text{Li}_3\text{AlF}_6$  is obtained [5]. The  $\alpha$  form seems to be stable up to 225 °C; but when heated above this temperature, the  $\beta$  form slowly appears. The reverse transformation has not been observed [7]. From x-ray powder pattern data, Garton and Wanklyn [5] have indexed  $\alpha$ - and  $\beta$ - $\text{Li}_3\text{AlF}_6$  on the basis of hexagonal unit cell; more recently Burns et al. [21] indexed  $\alpha$ - $\text{Li}_3\text{AlF}_6$  on the basis of orthorhombic unit cell.

## 2. Sample

The  $\text{Li}_3\text{AlF}_6$  sample, furnished by the Oak Ridge National Laboratory (ORNL) through the courtesy of R. E. Thoma and G. M. Hebert, had been prepared by fusing stoichiometric proportions of LiF and anhydrous  $\text{AlF}_3$  in a graphite crucible. The product was stated to be single phase by x-ray diffractometric and petrographic (microscopic) examinations and to contain 0.04 percent of water and 0.06 percent of oxygen from other oxygen-containing compounds. The sample was received in the form of a fused lump. The results of chemical analysis of a piece broken off the lump are summarized in table 1.

The analysis procedure for aluminum and lithium involved the dissolving of about a 0.2-g sample in sulfuric acid and heating to remove the fluorine as hydrogen fluoride. Aluminum was precipitated from the resulting solution as aluminum hydroxide with  $\text{NH}_4\text{OH}$ . The precipitate was filtered, ignited, and weighed as  $\text{Al}_2\text{O}_3$ . The filtrate was evaporated to dryness with  $\text{H}_2\text{SO}_4$  and the residue weighed as  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . The sodium was determined by flame photometry and the lithium was determined by difference.

The analysis for fluorine was similar to the procedure described by Hoffman and Lundell [8]. About 0.2 g of the sample was fused with anhydrous sodium carbonate and the cooled material transferred to a Claissen flask and dropping funnel system assembled for distillation. The fused material was dissolved in sulfuric acid (1–1 mixture) added from the dropping funnel. The solution was boiled at about 160 °C, adding small amounts of water through the dropping funnel whenever the temperature rose to about 170 °C. The distillate, containing the fluorine as fluorosilicic acid, was collected in a

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Chemical analysis of  $\beta$ -lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$ \*

Element	Percentage by Weight		
	Analysis		Theoretical
	Individual	Mean	
Li	12.87 12.94 12.95	12.92	12.87
Na	0.12 0.07	0.10	0
Al	16.68 16.79	16.74	16.68
F	70.29 70.56	70.42	70.45
Sum		100.18	100.00

\* Analyzed by E. June Maienthal and R. A. Paulson, NBS Applied Analytical Research Section.

solution of sodium hydroxide. The solution was evaporated to about 250 cm<sup>3</sup> and the fluoride was precipitated as  $\text{PbClF}$  from the solution. Next, the  $\text{PbClF}$  precipitate was dissolved in dilute nitric acid and the chlorine determined by the Volhard method. The amount of fluorine was computed from the corresponding chlorine equivalence.

The fused sample as received from ORNL had some outer areas of black coloration. Most of the black surface material was removed by scraping and the remaining sample was crushed to particle sizes between 0.5 to 2 mm on the edge and thoroughly mixed (all of the handling being done in an argon-atmosphere dry box with the dew point at about  $-80^\circ\text{C}$ ). Only minute amounts of black flecks remained in the sample. Of the original sample of about 200 g, 162.6555 g were used for the low-temperature heat-capacity measurements. The remainder, packaged in 1-g or 10-g units sealed in polyethylene bags, was reserved for high-temperature relative enthalpy measurements and for any additional analyses. The samples sealed in polyethylene bags were in turn placed in separate jars sealed with polyethylene snap-caps and stored in a desiccator containing magnesium perchlorate.

X-ray diffractometric examination of one of the 1-g samples was made by H. E. Swanson of the Crystallography Section of the National Bureau of Standards. The diffraction pattern was found to correspond to the low-temperature  $\beta$ - $\text{Li}_3\text{AlF}_6$  phase reported by Garton and Wanklyn [5]; no characteristic strong lines of  $\alpha$ - $\text{Li}_3\text{AlF}_6$  were observed. X-ray examination of the material after the heat-capacity measurements showed no change in the diffraction pattern.

The sample was analyzed spectrochemically after the heat-capacity measurements. The results of the analysis are summarized in table 2.

TABLE 2. Spectrochemical analysis of  $\beta$ -lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$ \*

Element	Percentage Limits By Weight	Element	Percentage Limits By Weight
Ag	< 0.001	Mg	0.001 - 0.01
Ba	< 0.001	Mn	< 0.001
Be	< 0.001	Na	0.1 - 1
Ca	0.001 - 0.01	Ni	<sup>a</sup> 0.1 - 1
Cr	0.001 - 0.01	Pb	< 0.001
Cs	< 0.001	Rb	< 0.001
Cu	< 0.001	Si	< 0.001
Fe	0.01 - 0.1	Sn	< 0.001
Ga	0.001 - 0.01	Ti	0.001 - 0.01
K	< 0.001		

\* Analyzed by Virginia C. Stewart, NBS Spectrochemical Analysis Section.

<sup>a</sup> A second spectrochemical analysis showed 0.01 to 0.1 percent nickel; chemical analysis showed 0.04 percent nickel.

The high nickel impurity content was unexpected and was considered highly improbable to have been introduced anywhere during the crushing and other handling processes employed in preparing the sample for the measurements. Since the original chemical analysis for lithium as  $\text{Li}_2\text{SO}_4$  could have included  $\text{NiSO}_4$ , a separate chemical analysis was made for nickel. Two  $\text{Li}_3\text{AlF}_6$  samples of about 0.6 g each were dissolved in water and perchloric acid. As a control, 0.500 mg of nickel was added to one of the samples. The nickel content of the solution was then determined spectrophotometrically using the dimethylglyoxime color reaction. The nickel found was 0.04 weight percent. Since the first spectrochemical analysis was on a small sample, a second spectrochemical analysis was made on a portion of a large  $\text{Li}_3\text{AlF}_6$  sample thoroughly mixed by grinding. The nickel analysis was 0.01 to 0.1 percent.

These analyses for nickel indicate that the  $\text{Li}_3\text{AlF}_6$  sample could be somewhat inhomogeneous. Since the crushed sample was thoroughly mixed and the sample size used in the chemical analysis was relatively large, the nickel content found by chemical analysis is considered most likely to be representative of the sample. Except for the small amount of sodium found in the sample, the analyses obtained agree with the theoretical values within the precision of the analytical procedure. Since the sodium content is low and is most likely present as  $\text{Na}_3\text{AlF}_6$ , the sample was taken to be 100 percent  $\beta$ - $\text{Li}_3\text{AlF}_6$  and no correction was made to the observed values of heat capacity for composition.

### 3. Apparatus and Method

The measurements were made using the calorimeter to be described in the paper on beryllium nitride ( $\text{Be}_3\text{N}_2$ ) [9]. Since a calibrated thermometer was used in the sample vessel, the thermometer-calibration feature built into the calorimeter was not used in the measurements.

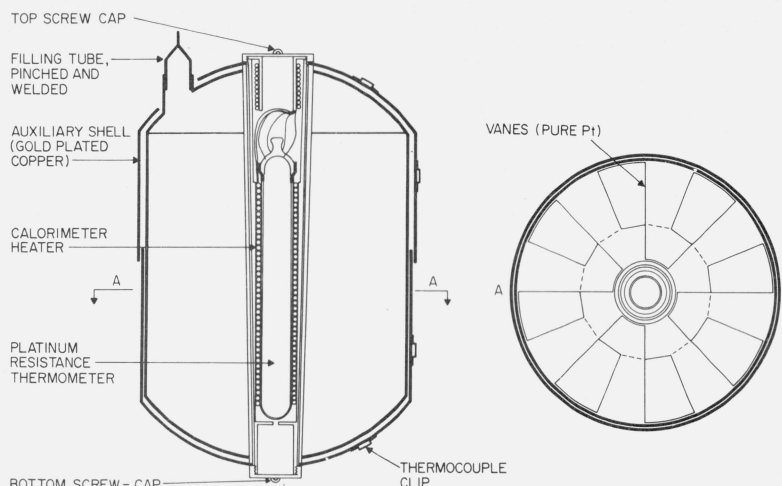


FIGURE 1. Calorimeter sample vessel system with platinum-iridium alloy vessel, central removable platinum resistance thermometer-heater assembly, and auxiliary outer copper shells.

A platinum-iridium alloy vessel, with pure platinum vanes to enhance temperature equilibrium, contained the  $\text{Li}_3\text{AlF}_6$  sample. Figure 1 shows a schematic representation of the calorimeter vessel system. The vertical platinum vanes, shown bent and arranged radially in the figure, were spot-welded at numerous places along the wall and the central tapered tube. The "floating" portion of the vanes was confined by bending the upper and lower half sections in opposite directions, shown by the alternate solid and dashed lines, respectively. The internal taper of the central tube was "finished" after the welding by reaming and lapping to a high polish.

The removable platinum-thermometer-heater assembly had a taper that closely matched the taper of the central tube. The calorimeter heater (100  $\Omega$ ), wound tightly on the platinum thermometer and cemented with epoxy resin, was a nickel-chromium alloy wire of low temperature-coefficient of resistance [10]. The combination was encased in a thin layer of tin-lead eutectic solder within the stainless steel tapered insert. The heater was "centrally" located in the insert so that its two ends would be nearly equally heated. The gold-plated outer auxiliary shells of copper were clamped to the vessel at the top and bottom with screwcaps as shown; the shells telescoped within each other at the middle. The calorimeter vessel system was suspended within the adiabatic shield of the calorimeter by means of a nylon cord [9]. Tests during the heating periods showed that the average temperatures of the two auxiliary shells differed at most about 0.02 K.

The following steps were taken in assembling the calorimeter vessel system: A thin layer of stopcock grease was applied to the parts of the tapered insert, calorimeter vessel, auxiliary shells, and screwcaps that were to be in mechanical contact. The lower auxiliary shell was first clamped to the vessel with the bottom screwcap, drawing the tapered thermometer-heater assembly tightly into the tapered central tube

of the vessel. The upper auxiliary shell was then clamped to the vessel with the top screwcap.

The same order was followed in the disassembly of the vessel system. After removing the lower auxiliary shell and the bottom screwcap, the top screwcap was tightened to loosen the tapered thermometer-heater assembly from the vessel. The upper auxiliary shell and thermometer-heater assembly were removed as a unit and could be later separated by loosening the screwcap. Actually, the upper auxiliary shell and the thermometer-heater insert were left intact and the top screwcap loosened when the insert was being reinstalled in the tapered tube of the calorimeter vessel.

The sample was introduced through a platinum filling tube (about 0.6 cm i.d.) gold-soldered into an auxiliary tubular opening on the vessel. The filling was done in a dry box (argon atmosphere; dew-point: about  $-80^\circ\text{C}$ ). After filling, the sample was pumped and purged several times with helium gas through the filling tube and finally sealed by pinching a 2-cm section of the platinum tube (previously annealed) flat, then simultaneously severing and sealing the tube at the middle of the flattened portion with an acetylene torch. A small amount<sup>2</sup> (8770  $\text{N/m}^2$ ) of helium gas was sealed in the vessel with the sample to help achieve rapid thermal equilibrium.

The platinum resistance thermometer (laboratory designation: 1066756) employed in the measurements was calibrated in accordance with the International Practical Temperature Scale of 1968 [12]. The temperatures  $T$  given in this paper correspond identically to the International Practical Kelvin Temperatures referred to with the symbol  $T_{68}$  in the above reference in kelvin units (symbol K).

The thermometer resistance measurements were made to the nearest 0.00001  $\Omega$  using initially a manual

<sup>2</sup> The observed pressure was initially expressed and the heat data processed in terms of mm Hg at  $0^\circ\text{C}$  and standard gravitational acceleration of  $980.665\text{ cm/s}^2$ . The conversion to  $\text{N/m}^2$  was made using the definition: 1 normal atmosphere =  $101,325\text{ N/m}^2 = 760\text{ torr}$  (mm Hg at  $0^\circ\text{C}$  and  $980.665\text{ cm/s}^2$ ) [11].

and later an automatic Mueller bridge. The observations with the automatic Mueller bridge [13, 14] were recorded automatically on punched cards and processed on a high-speed digital computer. In both manual and automatic methods the platinum thermometer resistances  $R_i$  and  $R_f$  were obtained, corresponding to before and after the introduction of a measured energy increment  $\Delta Q$ . The process used to reduce these observations to values of heat capacity at evenly spaced integral temperatures will be described later.

The electrical power introduced into the calorimeter heater was determined by manual measurements, using a Wenner potentiometer in conjunction with a volt box, standard resistor, and saturated standard cells, which were all calibrated at the National Bureau of Standards. A constant current source stable to about 2 ppm or better minimized current fluctuations. By using the Ni-Cr alloy wire mentioned earlier for the calorimeter heater, the total change of the heater voltage was not more than 0.05 percent during any heating period; for most of the measurements the total change was about 0.02 percent.

The heating interval was determined by means of a high-precision interval timer operated on the 60-Hz frequency standard provided at the National Bureau of Standards and stable to 0.5 ppm. As a check, an electronic counter containing a temperature-controlled 1-MHz calibrated quartz oscillator was also simultaneously employed in the measurement of the heating time interval. The estimated uncertainty in the determination of the heating time interval was not greater than  $\pm 0.01$  s for any heating period, none of which was less than 2 min in these experiments.

The calorimeter heater circuit was the same as that previously described [15]. Because of the short time constant of the constant current supply system, a make-before-break action was used in the calorimeter heater-dummy heater switch [14]. The energy increment ( $\Delta Q$ ), introduced during the heating period, was determined as the product ( $e i \tau$ ) of the heating time interval ( $\tau$ ), the average voltage drop ( $e$ ) across the calorimeter heater, and the current flow ( $i$ ) through the heater [15]. The average  $e$  and  $i$  were obtained from the observations, made at equally spaced time intervals (1 or 0.5 min) during the heating period. As mentioned earlier, the observed values of  $i$  were essentially constant and  $e$  usually changed about 0.02 percent during the heating period.

The 1961 atomic weights based on carbon 12 were used to convert the mass of  $\text{Li}_3\text{AlF}_6$  investigated to gram formula weight basis [16]. The energy measurements were made in terms of the mksa unit of energy, the joule. Whenever conversion to calorie was made, the following relation was used: 1 calorie = 4.1840 J.

#### 4. Results

Two series of measurements were made: one on the calorimeter vessel with sample (gross) and the other on the empty vessel (tare). The method of data reduction (to obtain smoothed values of heat capacity of  $\text{Li}_3\text{AlF}_6$  from the measured energy increments  $\Delta Q$

and the corresponding thermometer resistances  $R_i$  and  $R_f$  before and after heating, respectively) was similar to that described previously [17]. In principle, the procedure was to obtain  $dQ/dR$  of the sample (net) as a function of the thermometer resistance  $R$ . From the  $R$  versus  $T$  calibration and  $dR/dT$  for the thermometer, the heat capacity  $dQ/dT$  was calculated according to the relation:

$$dQ/dT = (dQ/dR) (dR/dT). \quad (1)$$

Briefly, the steps in the procedure were as follows: The measurements on the empty vessel represented by

$$\Delta Q = \int_{R_i}^{R_f} f(R) dR \quad (2)$$

were analyzed on a high-speed digital computer to obtain

$$dQ/dR = f(R). \quad (3)$$

The function  $f(R)$  used in analyzing the present measurements was a polynomial in  $(\ln R)/R$ , i.e.,

$$f(R) = \sum_{n=0}^N a_n ((\ln R)/R)^n. \quad (4)$$

The coefficients of eq (4) were obtained by the method of least squares using double precision calculations (16 to 17 figure accuracy). Experimental data obtained between about 15 and 380 K on the empty vessel are shown in figure 2 to be, except for a few points, within about  $\pm 0.04$  percent of the fifteenth-degree polynomial equation (eq (4),  $n=0$  to  $n=15$ ) fitted to the data (92 observations).

The polynomial equation for the measurements on the empty vessel was then evaluated to obtain values of  $\Delta Q$  (tare) corresponding to the thermometer resistance intervals ( $R_i$  and  $R_f$ ) observed for the gross measurements in order to obtain the energy increments for sample only, i.e.,

$$\Delta Q(\text{sample}) = \Delta Q(\text{gross}) - \Delta Q(\text{tare}). \quad (5)$$

The values of  $\Delta Q$  (sample and their corresponding values of  $R_i$  and  $R_f$ ) were fitted by the method of least squares to a polynomial equation of the form given also by eq (4). Figure 3 shows the deviation of the sample data (182 observations) from the final smoothed values based on a seventeenth-degree polynomial equation (eq (4),  $n=0$  to  $n=17$ ). The values of heat  $dQ/dT$  for the sample were calculated using eq (1), from  $dQ/dR$  evaluated from the polynomial equation at values of  $R$  corresponding to integral values of temperature  $T$  and from  $dR/dT$  of the platinum resistance thermometer. The values of  $dQ/dT$  were calculated from 15 to 380 K at 5 K intervals. (These values of  $dQ/dT$  will hereafter be referred to as experimental values).

In all of these calculations the second and third derivatives of the polynomial equations were examined



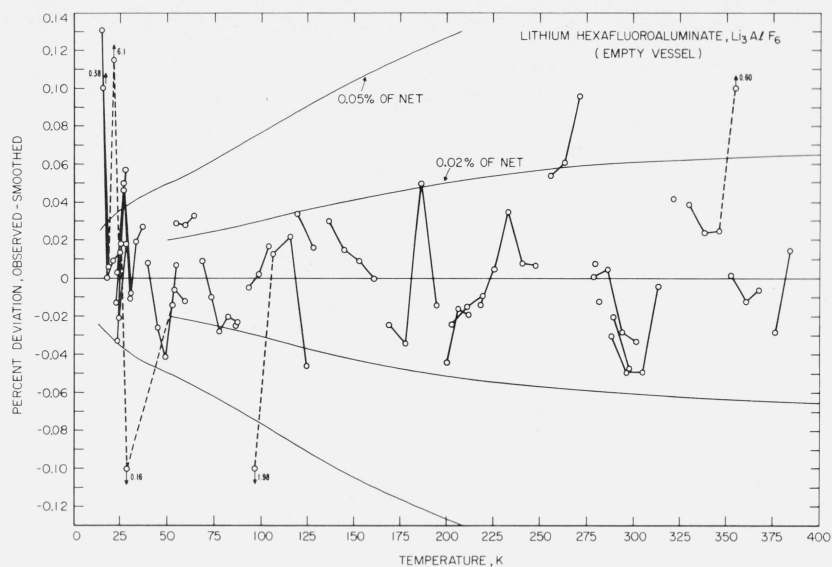


FIGURE 2. Deviation of empty-vessel measurements from polynomial equation:

$$dQ/dR = \sum_{n=0}^{15} a_n (\ln R/R)^n,$$

*fitted to the data.*

Consecutive measurements obtained during the day are connected by lines.

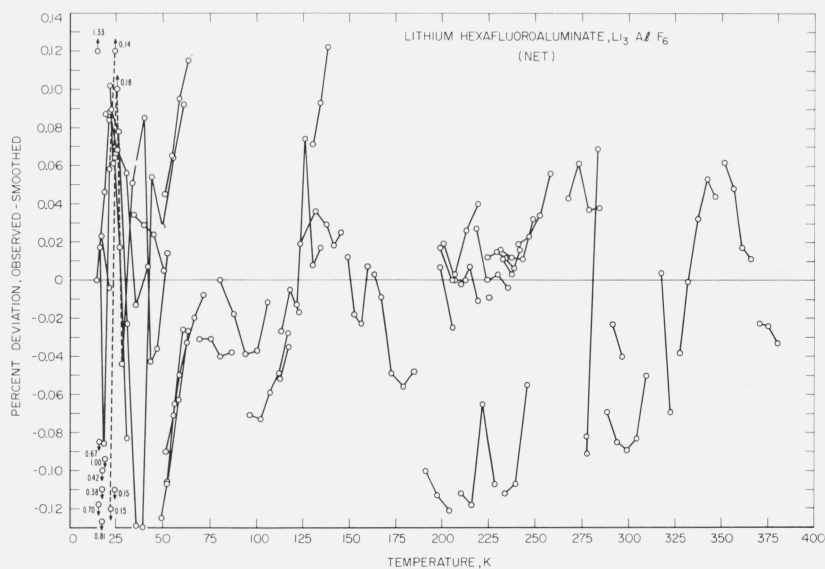


FIGURE 3. Deviation of the sample data (net) from polynomial equation:

$$dQ/dR = \sum_{n=0}^{17} a_n (\ln R/R)^n,$$

*fitted to the data.*

Consecutive measurements obtained during the day are connected by lines.

closely to ascertain that the equations "behave" in a manner expected of  $dQ/dR = f(R)$  [17].

The values of heat capacity below the experimental range (lower limit = 15 K) were obtained by graphical extrapolation to 0 K of  $C/T^3$  versus  $T$  plot of experimental values between 15 and 50 K. A slight adjustment (0.1 percent) was made to the experimental values around 20 to 25 K in order that the values of heat capacity between 0 and 50 K be smooth. The adjustment is within the scatter of the data (fig. 3) and the uncertainty in the  $dR/dT$  of the thermometer.

Considering the precision of the measurements, the possible systematic errors, and impurities in the sample, the estimated uncertainty<sup>3</sup> of the final smoothed values of heat capacity is 0.2 percent above 100 K. Below 100 K, because of the diminution in the thermometer sensitivity and in the relative fraction of the net over the gross heat capacity, the estimated uncertainty is 1 percent at the lower temperature limit (15 K) of the measurements. Because of the relatively poor thermal conductivity of platinum-iridium alloy as compared with copper, the time for "temperature equilibrium" was, with helium gas sealed in the vessel, about 30 to 40 min after the termination of heating. About one-half the time is required with all-copper vessels.

The smoothed values of heat capacity from 0 to 380 K were then used to calculate the thermodynamic properties using the relations:

$$H_T - H_0^c = \int_0^T C dT, \quad (6)$$

$$S_T = \int_0^T (C/T) dT, \quad (7)$$

and

$$G_T = H_0^c = (H_T - H_0^c) - TS_T. \quad (8)$$

The values of  $(H_T - H_0)/T$  and  $(G_T - H_0^c)/T$  were obtained by dividing the values of  $(H_T - H_0^c)$  and  $(G_T - H_0^c)$  obtained in eqs (6) and (8), respectively, by the appropriate temperature  $T$ . The values of thermodynamic properties are listed in table 3.

Greene, Gross, and Hayman [7] calculated  $S_{298} = 45 \text{ cal/K} \cdot \text{mol}$  for  $\alpha\text{-Li}_3\text{AlF}_6$  from the results of their heats of reaction measurements combined with vapor-equilibrium data and the relative enthalpy data reported by Douglas and Neufer [1]. The value agrees very favorably with the more accurate result  $44.904 \pm 0.090 \text{ cal/K} \cdot \text{mol}$  obtained in the present work. (Mixture of  $\alpha$  and  $\beta$  phases of  $\text{Li}_3\text{AlF}_6$  were obtained in the chemical combination reaction of LiF and

$\text{AlF}_3$  studies by Greene et al. Because of the slowness of conversion from  $\alpha$  to  $\beta$  phase, the heat of reaction was taken by Greene et al. to be equally applicable to either phase).

Douglas and Neufer [1] reported enthalpy measurements (relative to 0 °C) up to 800 °C on the same  $\text{Li}_3\text{AlF}_6$  sample. In table 4, their measurements at 323.15 K (50 °C) and 373.15 K (100 °C) are compared with the corresponding values given in table 3 based on the heat-capacity measurements obtained in the present work. The deviations of the values of enthalpy increments calculated using the enthalpy equation, derived by Douglas and Neufer [1] from their experimental data between 273.15 and 743.15 K, are in good agreement with the values from the heat-capacity measurements; the deviations of their mean observed values are, however, almost an order of magnitude greater and are of opposite signs. The good agreement between the present work and the values from the enthalpy equation based on the data between 273.15 and 743.15 K seems, therefore, somewhat fortuitous. The individual observations reported by Douglas and Neufer [1] also show wide scatter, probably because of varying amounts of  $\alpha$ - and  $\beta$ - $\text{Li}_3\text{AlF}_6$  being formed in the "drop" experiments.

The heat capacities of the mixed metal oxide compounds  $\text{BeO} \cdot \text{Al}_2\text{O}_3$  [18] and  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  [19] were found to exhibit positive deviation from those obtained by simple addition of heat capacities of the oxide components. In the region from 200 to 400 K the deviation from "additivity" is only 1 or 2 percent. At the lower temperatures, the deviation increases with decreasing temperature. At room temperature, only where enough data were available for comparison, the deviation from additivity of the heat capacities was found to be analogous to the deviation from additivity of the molal volumes of the oxides [19].

Figure 4 shows a positive deviation from additivity of the heat capacity of  $\text{Li}_3\text{AlF}_6$ . For  $\text{Na}_3\text{AlF}_6$ , the deviation from additivity is found to be only  $\pm 0.1$  percent between 180 and 360 K, the negative deviation being between 200 and 260 K [20]. The estimated uncertainty of the data in the temperature range is, however,  $\pm 0.3$  or  $\pm 0.4$  percent. The general shape of the deviation curves is similar to those found for  $\text{BeO} \cdot \text{Al}_2\text{O}_3$  and  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  [18, 19]. The minimum in the deviation is around 220 K for  $\text{Li}_3\text{AlF}_6$ , while those for  $\text{BeO} \cdot \text{Al}_2\text{O}_3$  and  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  occur at higher temperatures.

At room temperature, the deviation from additivity of the molal volume of  $\text{Li}_3\text{AlF}_6$  is about 5.6 percent and of the heat capacity about 1 percent, and of  $\text{Na}_3\text{AlF}_6$  about 5 and 0.05 percent, respectively. The deviation from additivity of the molal volume of  $\text{BeO} \cdot \text{Al}_2\text{O}_3$  is about 1.2 percent and of  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  about 4 percent, with the deviation from additivity of the heat capacity being about 1 percent for both mixed metal oxides.

These results seem to indicate that the additivity of heat capacities and molal volumes of mixed metal oxides and fluorides behave similarly. Additional data are needed to determine whether this relation holds over a broader range of temperatures.

<sup>3</sup> The uncertainty as used in this paper is an estimate reached by examining contributions to the inaccuracy from imprecision and possible systematic errors in the measurements. The authors estimate that there is a fifty-fifty chance that the error is no larger than that indicated.

TABLE 3. *Thermodynamic functions for  $\beta$ -lithium hexafluoroaluminate ( $\text{Li}_3\text{AlF}_6$ ) solid phase*

1 Mole = 0.1617889 Kg

$TK = 273.15 + t^\circ\text{C}$

$T$	$C_p^\circ$	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
$K$	$J/K\text{-mol}$	$J/\text{mol}$	$J/K\text{-mol}$	$J/K\text{-mol}$	$J/\text{mol}$	$J/K\text{-mol}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	.019	.024	.005	.006	.008	.002
10.00	.160	.391	.039	.052	.128	.013
15.00	.604	2.116	.141	.186	.673	.045
20.00	1.664	7.458	.373	.486	2.263	.113
25.00	3.577	20.201	.808	1.047	5.970	.239
30.00	6.275	44.542	1.485	1.927	13.267	.442
35.00	9.573	83.947	2.398	3.135	25.789	.737
40.00	13.307	141.00	3.525	4.653	45.137	1.128
45.00	17.355	217.54	4.834	6.452	72.789	1.618
50.00	21.654	314.97	6.299	8.501	110.07	2.201
55.00	26.146	434.40	7.898	10.774	158.17	2.876
60.00	30.782	576.67	9.611	13.247	218.14	3.636
65.00	35.542	742.43	11.422	15.898	290.94	4.476
70.00	40.414	932.27	13.318	18.709	377.39	5.391
75.00	45.387	1146.7	15.290	21.667	478.27	6.377
80.00	50.444	1386.3	17.329	24.757	594.28	7.429
85.00	55.560	1651.3	19.427	27.968	726.05	8.542
90.00	60.712	1941.9	21.577	31.290	874.15	9.713
95.00	65.875	2258.4	23.773	34.711	1039.1	10.938
100.00	71.031	2600.7	26.007	38.221	1221.4	12.214
105.00	76.157	2968.7	28.273	41.811	1421.5	13.538
110.00	81.234	3362.2	30.565	45.471	1639.6	14.906
115.00	86.249	3780.9	32.877	49.193	1876.3	16.315
120.00	91.191	4224.5	35.205	52.968	2131.6	17.764
125.00	96.049	4692.7	37.541	56.790	2406.0	19.248
130.00	100.82	5184.9	39.884	60.650	2699.6	20.766
135.00	105.49	5700.7	42.227	64.543	3012.6	22.315
140.00	110.05	6239.6	44.568	68.462	3345.1	23.893
145.00	114.51	6801.0	46.904	72.402	3697.2	25.498
150.00	118.87	7384.5	49.230	76.358	4069.1	27.127
155.00	123.10	7989.5	51.545	80.325	4460.8	28.779
160.00	127.23	8615.4	53.846	84.298	4872.4	30.452
165.00	131.24	9261.6	56.131	88.275	5303.8	32.144
170.00	135.14	9927.6	58.398	92.251	5755.1	33.854
175.00	138.93	10612.	60.645	96.224	6226.3	35.579
180.00	142.60	11316.	62.871	100.19	6717.4	37.319
185.00	146.16	12038.	65.074	104.15	7228.2	39.071
190.00	149.61	12778.	67.253	108.09	7758.8	40.836
195.00	152.95	13534.	69.408	112.02	8309.1	42.611
200.00	156.18	14307.	71.57	115.93	8878.9	44.395
205.00	159.31	15096.	73.640	119.83	9468.4	46.187
210.00	162.35	15900.	75.716	123.70	10077.	47.987
215.00	165.28	16719.	77.765	127.56	10705.	49.792
220.00	168.12	17553.	79.786	131.39	11352.	51.603
225.00	170.87	18400.	81.780	135.20	12019.	53.419
230.00	173.53	19261.	83.746	138.98	12704.	55.238
235.00	176.10	20135.	85.684	142.74	13409.	57.060
240.00	178.60	21022.	87.593	146.48	14132.	58.884
245.00	181.01	21921.	89.475	150.18	14873.	60.709
250.00	183.35	22832.	91.330	153.87	15633.	62.535
255.00	185.62	23754.	93.156	157.52	16412.	64.362
260.00	187.82	24688.	94.956	161.14	17209.	66.188
265.00	189.95	25632.	96.728	164.74	18023.	68.014
270.00	192.01	26587.	98.474	168.31	18856.	69.838

TABLE 3. *Thermodynamic functions for  $\beta$ -lithium hexafluoroaluminate ( $\text{Li}_3\text{AlF}_6$ ) solid phase—Continued*

$T$	$C_p^\circ$	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
273.15	193.28	27194.	99.560	170.55	19390.	70.987
275.00	194.01	27553.	100.19	171.85	19706.	71.661
280.00	195.96	28527.	101.89	175.37	20574.	73.482
285.00	197.84	29512.	103.55	178.85	21460.	75.300
290.00	199.66	30506.	105.19	182.31	22363.	77.115
295.00	201.44	31509.	106.81	185.74	23283.	78.927
298.15	202.53	32145.	107.82	187.88	23871.	80.067
300.00	203.16	32520.	108.40	189.14	24220.	80.736
305.00	204.84	33540.	109.97	192.51	25174.	82.540
310.00	206.47	34568.	111.51	195.85	26145.	84.341
315.00	208.06	35605.	113.03	199.17	27133.	86.137
320.00	209.61	36649.	114.53	202.46	28137.	87.929
325.00	211.12	37701.	116.00	205.72	29157.	89.716
330.00	212.59	38760.	117.46	208.95	30194.	91.499
335.00	214.03	39827.	118.89	212.16	31247.	93.276
340.00	215.43	40900.	120.30	215.34	32316.	95.047
345.00	216.80	41981.	121.69	218.50	33400.	96.814
350.00	218.14	43068.	123.05	221.63	34501.	98.574
355.00	219.45	44162.	124.40	224.73	35617.	100.33
360.00	220.74	45263.	125.73	227.81	36748.	102.08
365.00	222.00	46370.	127.04	230.86	37895.	103.82
370.00	223.23	47483.	128.33	233.89	39056.	105.56
373.15	223.99	48187.	129.14	235.79	39796.	106.65
375.00	224.44	48602.	129.61	236.90	40233.	107.29
380.00	225.62	49727.	130.86	239.88	41425.	109.02

$H_0^\circ$  and  $S_0^\circ$  apply to the reference state of the solid at zero K.

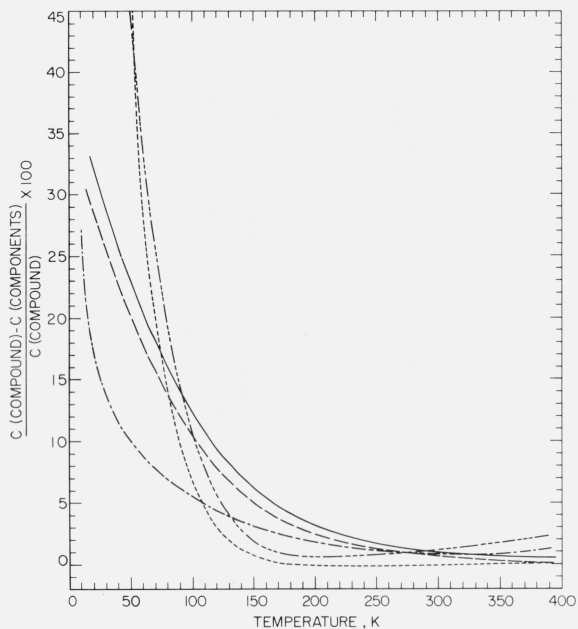


FIGURE 4. *Comparison of the additivity of heat capacities.*

—  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  versus  $\text{BeO} + 3\text{Al}_2\text{O}_3$   
 ---  $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$  versus  $\text{BeO} \cdot \text{Al}_2\text{O}_3 + 2\text{Al}_2\text{O}_3$   
 - · -  $\text{BeO} \cdot \text{Al}_2\text{O}_3$  versus  $\text{BeO} + \text{Al}_2\text{O}_3$   
 .....  $\text{Li}_3\text{AlF}_6$  versus  $3\text{LiF} + \text{AlF}_3$   
 - - - -  $\text{Na}_3\text{AlF}_6$  versus  $3\text{NaF} + \text{AlF}_3$

TABLE 4. *Comparison of enthalpy differences obtained on  $\beta$ -lithium hexafluoroaluminate,  $\text{Li}_3\text{AlF}_6$*

Temperature interval	This work	Douglas and Neuffer [1]	
		Mean observed	Equation <sup>a</sup>
$K$	$J/\text{mole}$	$J/\text{mole}$	$J/\text{mole}$
273.15 to 323.15	10117	10156	10124
273.15 to 373.15	20994	20964	20996

<sup>a</sup> These values are from an enthalpy equation derived by Douglas and Neuffer [1]:

$$H_T^\circ - H_{273.15\text{ K}}^\circ = 64.1398T + 0.0070246T^2 - 13653.13 \log_{10}T + 15,220.6 \text{ in cal/mole for the interval } 273.15 \text{ to } 743.15 \text{ K.}$$

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